POLYMERIC NITROGEN: THE ULTIMATE, GREEN HIGH PERFORMING ENERGETIC MATERIAL

Jennifer A. Ciezak and Betsy M. Rice
U. S. Army Research Laboratory, AMSRD-ARL-WM-BD
Aberdeen Proving Ground, MD 21005-5069

ABSTRACT

High-energy-high-density materials that offer increased stability, vulnerability, and are environmentally safe are being aggressively pursued to meet the requirements of the DoD Joint Visions and Future Force. It was proposed nearly two decades ago, polymeric nitrogen would exceed all of these requirements, with energy release nearly five times that any conventional energetic material in use today. In this paper, we describe an experiment in which a meta-stable polymeric form of nitrogen has been synthesized under high-pressure using sodium azide as the starting material. Recent characterization and ideas for future work are discussed.

1. INTRODUCTION

In order to play a critical part in the DoD Joint Vision 2010 and Joint Vision 2020, the research and development communities face an unprecedented challenge to transform the Army into a force that can dominate the full spectrum of military operations. The evolution of smaller, lighter platforms for the Future Force with increased range and lethality presents a difficult challenge for the development of future munitions. The formulation of energetic materials used in these munitions is a key component that affects the survivability in both logistical (storage, transportation) and tactical (stowed on weapons platforms) environments. In order to meet these criteria and support the Joint operations, new energetic materials (EMs) with reduced sensitivity and vulnerability are being aggressively pursued. Focus is particularly strong for EMs that exceed both performance specifications and insensitive munitions requirements, and are environmentally safe. Novel energetic formulations are also of considerable interest to this program as they specifically offer the potential to tailor the dynamic release of energy, providing increased weapon efficiency and vulnerability while meeting the green munitions requirements.

Nearly two decades ago it was proposed that a singly bonded polymeric form of nitrogen would exceed all of these requirements. Nitrogen is commonly considered to be an inert material because the $N \equiv N$ triple bond is one of the most stable known [Greenword et al., 1984]. However, because nitrogen exhibits a uniquely large energy difference between that of the single bond (160 kJ/mol) and that of the triple bond (954 kJ/mol), nitrogen atoms arranged into a singly-bonded polymeric network will form a high-energy-density-material, if the material is metastable. Conversion from the singly-bonded form to the molecular state would release nearly five times the energy of any conventional energetic material in use today.

There have been extensive experimental searches for the polymeric form of nitrogen in the past few years [Eremets et al. 2001, 2004; Goncharov, 2000; Gregoryanz et al. 2002, 2004] under pressures up to 270 GPa and temperatures ranging from 10 – 2500 K. A black, non-molecular phase was first identified above 180 GPa at 80K [Eremets et al., 2001]. This high-pressure phase persists at room and elevated temperatures [Goncharov et al., 2000; Gregoryanz et al., 2002, 2004]. Several properties of the black phase are similar to those predicted for polymeric nitrogen and all optical data indicates an amorphous (non-molecular) phase but no convincing evidence exists for an extended nitrogen framework [Eremets, Gavriliuk et al., 2004]. Recently, an allotropic form of nitrogen was synthesized directly from molecular nitrogen at temperatures exceeding 2500K and pressures above 110 GPa [Eremets, Gavriliuk et al., 2004]. This phase can be quenched to ambient pressure due to the large hysteresis of the material, but only at low temperatures, precluding performance testing of the material [Eremets, Gavriliuk et al., 2004]. X-ray diffraction provides strong evidence for the cubic-gauche polymeric phase but cannot unequivocally confirm the structure of the material, due to the limited number of diffraction peaks that can be resolved.

There has been extensive theoretical debate about the stability of non-molecular polymeric phases of nitrogen at ambient conditions, particularly the cubic-gauche phase, shown in Figure 1 [Mattson et al., 2004]. Quantum mechanical (QM) calculations have been used to characterize and test the stability of high-pressure, non-molecular amorphous structures generated through quenching of hot atomic nitrogen gas. Destabilization of these structures begins upon decompression when adjacent singly-coordinated atoms within the nitrogen network break away to form diatomic molecules [Mattson et al. 2003]. 'Unraveling' propagates through the polymer and ultimately results in a back transformation to

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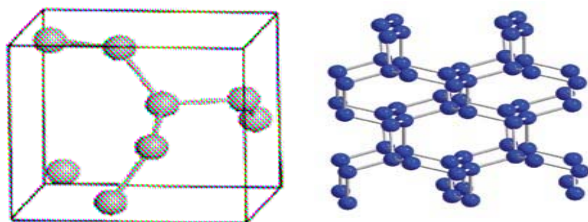| 16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
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Figure 1. Each atom of nitrogen is connected to three neighbors with three single covalent bonds. The primitive cell is shown (left), and an extended structure of the polymeric nitrogen is shown (right).

a molecular phase. QM calculations have shown that passivation of the terminal ends of the singly-coordinated atoms with an impurity, such as hydrogen or ammonia, produced an increase in the stability of the amorphous polynitrogen structures upon decompression [Mattson et al. 2003].

The present study details an investigation into nitrogen polymerization through a novel high-pressure approach using sodium azide (NaN_3) as the starting material. Due to the weaker bonding structure of the anionic azide chains (N_3^-) in comparison to a $N\equiv N$ bond, one expects that the N_3^- chains will create single-covalently bonded polymeric networks more easily than diatomic nitrogen. The absence of distinct Raman features in the NaN_3 spectrum at 120 GPa suggests a transition from a molecular phase to a polymeric nitrogen phase, which has the sodium cations interspersed throughout the network. Unfortunately, crystallographic characterization of this high-pressure phase is unavailable and upon return to ambient conditions, the material transforms back to a mixture of NaN_3 and two other new phases, which are stable at ambient conditions. Due to the difficulty of separating these phases, the crystal structures of these two new phases have not been resolved. Raman spectra of the mixture, however, have revealed the possibility of a polymeric phase interspersed with the other two phases [Eremets, Yu et al. 2004].

Using the computational simulations of the polymeric nitrogen mixed with hydrogen or ammonia gas as a guide, we have investigated the possible isolation of polymeric nitrogen using a sodium azide/ hydrogen mixture. Pure sodium azide mixed with hydrogen gas was pressurized to 40 GPa and characterized using Raman spectroscopy and x-ray diffraction. A non-reversible phase transition was observed at 19 GPa that persists upon pressure release and is stable at ambient conditions. X-ray diffraction obtained as a function of pressure implies this phase is inherently different from that of pure sodium azide. The analysis of the Raman spectra corroborates the non-molecular characteristics of this new

phase and suggests this material may be a phase in which the nitrogen atoms are arranged in a polymeric network. we have investigated the possible isolation of polymeric nitrogen using a sodium azide/ hydrogen mixture. Pure sodium azide mixed with hydrogen gas was pressurized to 40 GPa and characterized using Raman spectroscopy and x-ray diffraction. A non-reversible phase transition was observed at 19 GPa that persists upon pressure release and is stable at ambient conditions. X-ray diffraction obtained as a function of pressure implies this phase is inherently different from that of pure sodium azide. The analysis of the Raman spectra corroborates the non-molecular characteristics of this new phase and suggests this material may be a phase in which the nitrogen atoms are arranged in a polymeric network.

2. EXPERIMENTAL METHODS

Sodium azide (99.99 % pure) was obtained from Aldrich Chemical Company and used without further purification. Piston-cylinder type diamond anvil cells (DACs) were used for all experiments. The sodium azide sample was lightly ground into a fine powder and placed in a sample well pre-indented into a rhenium gasket of approximately 120 μm in diameter and a depth of 35 μm. The pressure was determined from the shift of the R_1 ruby fluorescence line with pressure, which is precise to ± 0.05 GPa under quasi-hydrostatic conditions [Mao et al., 1986]. Helium was used as the pressure medium for all experimental measurements. High-pressure Raman experiments were performed using the 488.0 nm line of an argon ion laser (Coherent Innova 90) as the excitation source, with output power kept at less than 0.1W. A 460-mm focal length f/5.3 imagining spectrograph (ISA HR 460) equipped with an 1800-grooves/mm grating with a resolution of $\pm$ 0.5 cm^{-1} was used. The wavelength calibration was performed using a neon light and has an accuracy of ± 1 cm^{-1}. Angle dispersive x-ray diffraction measurements using a focused synchrotron beam, HPCAT, Sector 16, Advanced Photon Source, were carried out in-situ at room temperature as a function of pressure. In the present experiments, the x-ray beam with a wavelength of 0.368 Å was collimated to 50 μm. The data were recorded on a MAR charge-coupled device (CCD) calibrated with a CeO_2 standard. The pressure was determined from the spectral shift of the R_1 ruby line with pressure.

3. RESULTS AND DISCUSSION

At ambient conditions, the azide chains (N_3^-) of the sodium azide molecule are arranged in layers perpendicular to the planes of the sodium atoms (see Figure 2). Since these ions only weakly interact with each other, this molecular configuration is unstable, and a
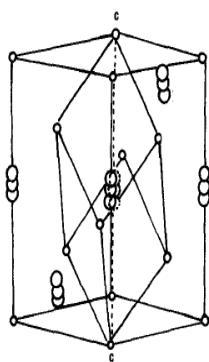
Figure 2. The crystal structure of NaN$_3$ under ambient conditions (β-NaN$_3$).

phase transition to α-NaN$_3$ has been observed at relatively low pressures. The azide chains in the α polymorph are tilted permitting stronger interactions between the neighboring chains and higher stability. In an attempt to understand the high-pressure behavior of the NaN$_3$/H$_2$ mixture, x-ray diffraction patterns were obtained on isothermal compression at room temperature. Representative x-ray diffraction patterns of NaN$_3$/H$_2$ are shown in Figure 3. We found good agreement with the reported results for the alpha phase with eight characteristic diffraction peaks below 20° at 0.5 GPa. Upon compression, the two sets of doublets at 7° and 11.5° shift at different rates as a function of pressure, resulting in four well-resolved diffraction peaks. The patterns above 15.4 GPa differ considerably from the original NaN$_3$/H$_2$ pattern. The

diffraction patterns observed at these pressures also differ from those of other alkali azide phases including CsN$_3$ [Iqbal et al., 1975] and LiN$_3$ [Pringle et al, 1968]. The abrupt broadening of the peaks at 21.0 GPa suggests a transition to a structure which has an increased amount of strain. The strain is retained upon decompression, suggesting this new phase is amorphous in nature. If this new phase is amorphous, further x-ray diffraction will only be of limited use. Future work will involve x-ray absorption fine structure (XAFS), which can provide information about the nearest neighbor interactions including the distance between the neighboring atoms. This technique has been used successfully to resolve the structure of amorphous carbon [Batson et al., 1979]

Further analysis of these diffraction patterns has been fraught with difficulties. The limited number of resolvable peaks in the diffraction pattern hampers an accurate refinement of the molecular positions and lattice constants. The narrow range of peaks observed is a direct result of the geometry of the diamond anvil cell, which is constructed such that there is a restriction in the number of Debye-Scherrer cones that can be probed at any time. Additionally, the limited number of diffraction peaks
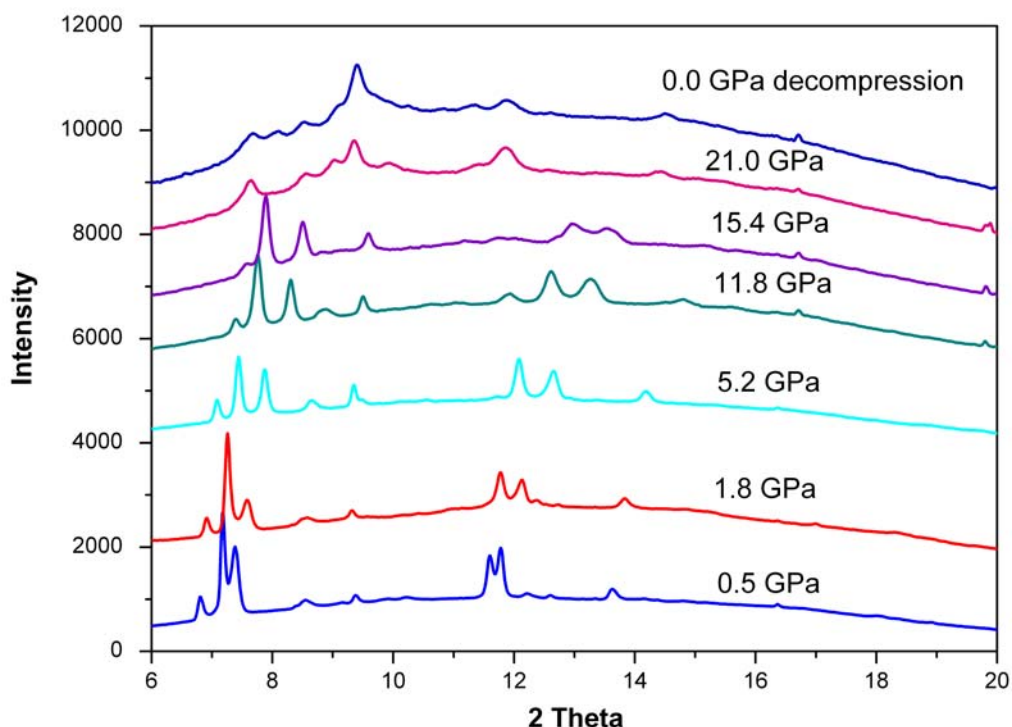

Figure 3. Typical examples of powder x-ray diffraction patterns of NaN$_3$/H$_2$ recorded under hydrostatic conditions. With increasing pressure, the peaks shift at different rates leading to well-resolved peaks. At 21.0 GPa, the peaks begin to broaden and a phase transition occurs.
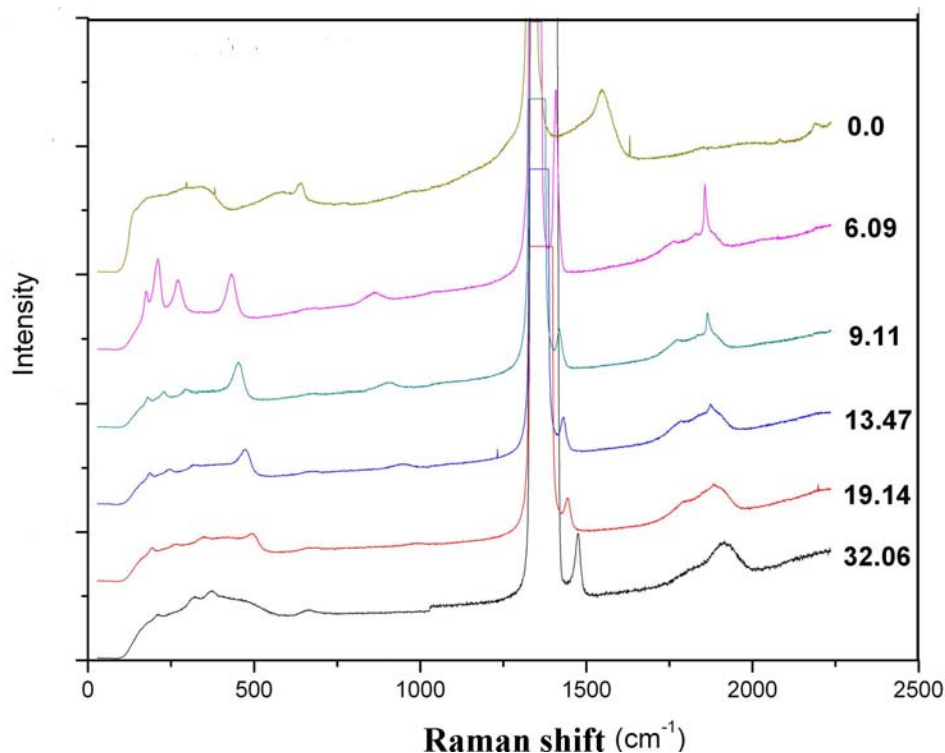
Figure 4. Selected Raman spectra of NaN_3/H_2 as a function of compression. Each spectrum is appropriately marked by a pressure value. The first order diamond scattering vibration (~1300 cm^{-1}) is truncated to allow for clarity of the lower intensity vibrational modes of sodium azide.

coupled with peak broadening impedes confirming the unit cell symmetry for the high-pressure phase. Experiments are currently underway using a specialized beryllium cell, which is virtually invisible to x-rays, permitting more Debye-Scherrer cones to be probed. The addition of these high-angle peaks to the existing patterns will hopefully aide in the derivation of further crystallographic information.

Several representative Raman spectra are shown in Figure 4. The spectrum recorded at 3.6 GPa compares favorably to the known spectra of α-NaN$_3$ [Iqbal, 1973; Simonis et al., 1974; Kanney et al., 1977] The three Raman active and six IR active vibrational modes of sodium azide have been extensively characterized experimentally. The symmetric stretching mode (ν$_1$) is observed in the Raman spectrum at approximately 1360 cm^{-1} while the two other fundamental bending (638 cm^{-1}) and asymmetric stretching (2090 cm^{-1}) modes are only discernable in the IR spectrum due to symmetry restrictions. [Eremets, Yu, et al. 2004] Although it is relatively unusual, it is well documented the first overtone of the IR-active bending mode (638 cm^{-1}) appears in the Raman spectrum at ~ 1268 cm^{-1}. The lattice region (0 – 300 cm^{-1}) of the Raman spectrum is dominated by one liberational mode (122 cm^{-1}) while three liberational modes are observed in the IR lattice region (175, 195 and 250 cm^{-1}).

The Raman spectral features remain consistent up to 14.8 GPa. At 14.8 GPa, a profoundly different Raman spectrum emerges which signifies the onset of a phase transition. The appearance of several IR active modes in the Raman spectrum indicates a lowering of the molecular symmetry accompanies this transition. The appearance of these new bands, accompanied by the splitting of the Raman active lattice mode, results in six low frequency modes. Upon further compression to 22.7 GPa, a new vibrational features emerges between 1700 – 1900 cm^{-1}. This band has been previously attributed to a strong coupling of the azide chains and possible formation of N$_4^+$ clusters [Eremets, Yu, et al. 2004]. While this band persists to the highest pressure studied in this report, no new vibrational features are observed in the Raman spectrum that indicate a complete transformation to a polymeric phase. In general, the Raman features 'smear out' as pressure is increased suggesting at 19 GPa the material loses long-range order and becomes amorphous and possibly non-molecular.

The behavior of high-pressure phase of sodium azide upon return to ambient conditions yields critical information on the physical and chemical properties of the phase transformation. As is shown in Figure 5, the high-pressure phase persists upon decompression to atmospheric pressure. Several vibrational changes were
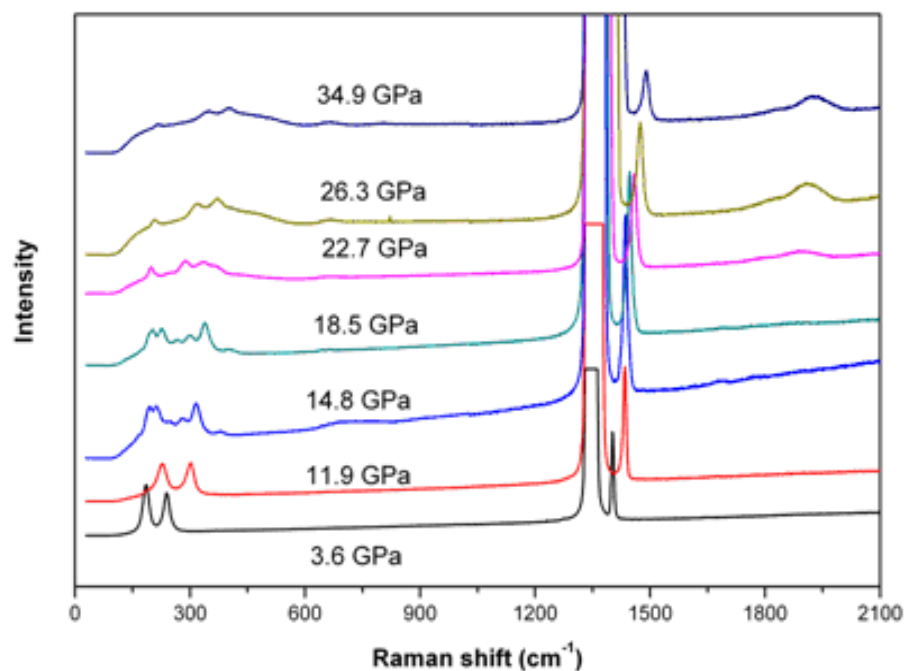
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Figure 5.   Representative Raman spectra of sodium azide on decompression.

observed over the course of the decompression studies, which indicate alterations in the structure of the phase may be necessary for the stabilization of the material at low pressures. The azide coupling vibration (1940 cm^{-1}) sharpens and an intensity increase is observed over the decompression sequence. This feature persists to 6.1 GPa and completely disappears at atmospheric pressure. This result is contrary to prior results in which the azide coupling vibrational mode remained resolvable at ambient conditions [Eremets, Yu, et al. 2004]. This behavior was interpreted as retention of the polymeric phase at ambient conditions.   At 6.1 GPa, the low frequency vibrations become distinguishable, but the vibrational pattern which emerges is not consistent with that of the compression sequence, indicating the physical and chemical properties of the high-pressure phase are inherently different from those of the starting material. Below 6.1 GPa, the material's behavior is rather complex and unusual in that all of the vibrational maxima again become 'smeared out' and several new vibrational features emerge: a broad doublet ca. ~750 cm^{-1}, a shoulder off the first order diamond vibration ca. ~1250 cm^{-1} to lower energy, and a relatively intense, broad band ca. 1600 cm^{-1}. Although the specific molecular motions associated with these bands have yet to be identified, these vibrational features are consistent with the bands used as evidence for formation of a non-molecular polymeric phase [Eremets, Yu, et al. 2004]. However, previously it was noted the polymeric material was not stable at ambient conditions, while the material synthesized in our experiment remains stable in laboratory conditions for at least two weeks. Additional

work is being done on this material as well as the conditions under which it was synthesized, in an effort to understand the role the hydrogen plays in this transformation and whether the material truly is polymeric in nature.

4. CONCLUSIONS

The high-pressure study of the sodium azide/H_2 mixture up to 40 GPa at room temperature revealed the formation of a high-pressure phase which is distinctly different from that of the starting material. This high-pressure phase first appears near 21 GPa and is characterized by the appearance of a vibration at ~ 1900 cm^{-1}, which has been attributed to an azide coupling mode. The azide coupling vibrational mode increased in intensity upon decompression suggesting the coupling strength increases as pressure decreases. As evidenced by x-ray diffraction and Raman spectroscopy, this phase persists to ambient pressure.

The pattern of the low frequency vibrations at 6.1 GPa is considerably different from that of the starting material, indicating this phase has inherently different properties than that of pure sodium azide. At 0 GPa, all vibrational features become 'smeared out' and several new features appear. The vibrational pattern present at ambient pressure is remarkably similar to that of the polymeric phase of sodium azide at 160 GPa [Eremets, Yu, et al. 2004]. Furthermore, while the previous report indicated the polymeric phase was unstable at ambient

conditions, our material is stable under laboratory conditions for at least two weeks.

While the Raman spectra provide strong evidence for the transformation of the sodium azide/H_2 mixture into a meta-stable polymeric form of nitrogen, further analysis is necessary to confirm the structure. Specialized x-ray diffraction and x-ray absorption fine structure experiments will be performed in the near future allowing further insight into the molecular structure of the material. Although much work remains to be done, these experiments have lead to important insight into the possible synthesis routes for a polymeric form of nitrogen.

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